

# National Textile Center

## FY 2003 (Year 12) Continuing Project Proposal

Project No. **C02-CD06**

Competency: **Chemistry**

### Chemistry of Functional Finishing: Self-decontaminating Materials

#### Project Team:

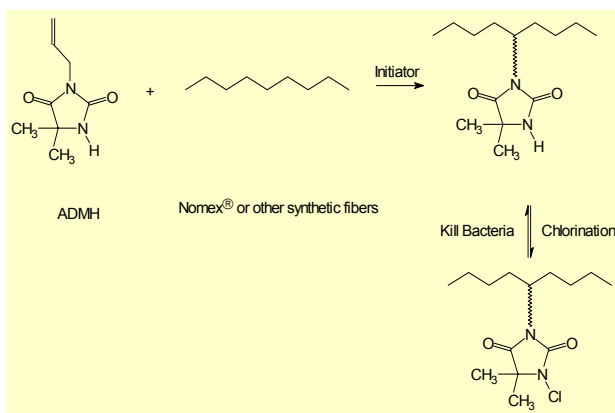
Leader: **Gang Sun/ UC Davis, textile and polymer chemistry, functional textiles**  
Email: [gysun@ucdavis.edu](mailto:gysun@ucdavis.edu) Phone: 530-752-0840  
Members **Roy Broughton Jr./ Textile Eng. Auburn/ [royalb@eng.auburn.edu](mailto:royalb@eng.auburn.edu) /fiber and polymer engineering**  
**Yuyu Sun/UCD/ [yysun@ucdavis.edu](mailto:yysun@ucdavis.edu) / textile and polymer chemistry**  
Collaborator: **Dr. Pengfei Gao, National Laboratory of Personal Protective Equipment, NIOSH**

#### Objective:

To develop a novel chemistry (a controlled radical grafting polymerization) method that can be universally applied in the chemical functional finishing of most textile materials, with a particular focus on developing functions on protective clothing that can self-decontaminate biological and chemical hazards.

#### Progress Statement:

The controlled radical grafting polymerization method is a novel chemical process proposed by the PI in functional finishing of textile materials, particularly synthetic fibers. The grafting reaction is a very useful tool in the chemical modification of fiber surfaces, which requires reactive sites on polymers but are mostly limited to cotton and a few fibers. In order to develop a universal grafting method that can be applied on most textile fibers including natural and synthetic, we believe only a radical grafting method will work with most of the materials. Traditionally, radical grafting reactions could happen when radical initiators, vinyl monomers, and textile fibers are coexisting in a solution. However, in such a system the grafting reaction of the monomer on fibers is a minor reaction, while the homopolymerization is the dominate one. Even when the grafting reaction starts on the fibers it will lead to a long chain grafting product; i.e. the monomers will form long side chains, which will affect the original properties of the fibers.



Scheme 1. ADMH grafting copolymerization and chlorination on the synthetic fibers

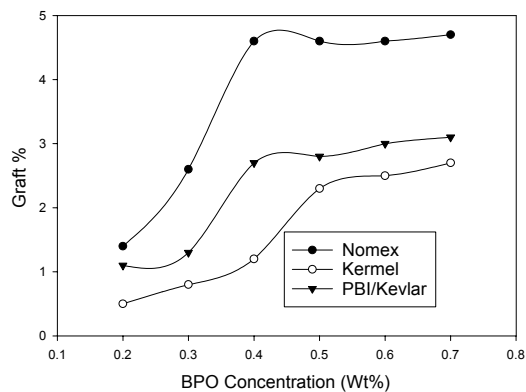


Figure 1. Influence of BPO on Graft%. Padding bath contained: ADMH, 3 wt%; PEG-DIA, 2 wt%

In our recent study, we have not only made the grafting reaction possible on most textile fibers, but also have completely solved the problems existing in the traditional grafting reactions. We have synthesized functional monomers and demonstrated successful chemical modifications of polyester, nylon, acrylics, Nomex, Kevlar and many other hydrophilic and hydrophobic fibers by using a controlled radical grafting reaction in convenient textile finishing processes. Again, to focus on self-decontaminating functions on clothing materials, we grafted specific

monomers containing hydantoin rings to all of the tested fibers with very good conversion yields. The fabrics revealed powerful biocidal functions against both Gram-negative and Gram-positive bacteria. The grafting reaction of a new monomer, 3-allyl-dimethylhydantoin, onto synthetic fibers is shown in Scheme 1.

The reactive allylic group instead of the vinyl group prevents chain propagation after the monomer radical is formed, thus ensuring a single monomer or short chain grafting reaction. Initiators, such as benzoyl peroxide (BPO), could preferably generate radicals on fiber surfaces rather than initiating monomers. With these two major components controlled in the reaction, the grafting yields were almost quantitative (Figure 1). The resulting fabrics demonstrated powerful and durable biocidal properties against *E. coli* and *S. aureus* (Table 1). The biocidal functions are fully rechargeable by using a chlorine bleach during the laundry process.

Table 1. Percentage Reduction of the bacteria after washing at a contact time of 60 min

Wash times	Nomex <sup>®</sup>			Kermel <sup>®</sup>			PBI <sup>®</sup> /Kevlar <sup>®</sup>		
	M <sub>Cl</sub> x10 <sup>5</sup> (mol/g)	E. coli	S. aureus	M <sub>Cl</sub> x10 <sup>5</sup> (mol/g)	E. coli	S. aureus	M <sub>Cl</sub> x10 <sup>5</sup> (mol/g)	E. coli	S. aureus
0	1.22	99.9999	99.9999	0.33	99.9	99.999	0.41	99.9	99.9999
5	1.20	99.9999	99.9999	0.28	99.9	99.99	0.41	99.9	99.99
15	0.63	99.9999	99.999	0.23	99.9	99	0.37	99.9	99
30	0.27	99.9	99.99	UD*	90	90	0.20	90	99
50	UD*	90	90	UD*	UD*	UD*	UD*	UD*	UD*
50**	1.14	99.9999	99.9999	0.29	99.9	99.999	0.43	99.9	99.9999

\*: no reduction was detected, and \*\*: these samples were re-bleached after 50 times of washing.

---

### Next Year's Goals:

The goals for the next two years are to continue the study on the controlled grafting finishing method on all synthetic fibers. The new method should be universally applicable to most textile fibers, should not alter the integrity of the original materials, and should be easy to implement in a convenient textile finishing system. We have achieved very promising results using a controlled radical grafting polymerization method, and have found proper reactive monomer and initiator structures that can meet the above requirements.

New monomer structures that can undergo the grafting reactions on most polymeric materials without the tendency of having self-polymerization in the textile finishing process will be synthesized. New initiators that can selectively generate radicals on fiber surfaces, rather than on monomers, will be explored as well.

Antimicrobial efficacy of the materials will be evaluated by using gram-positive and gram-negative bacteria. The durability and rechargeability of the functions will be examined following AATCC testing standards.

Another goal for the year is to explore functions of detoxifying toxic chemicals' oxidative decomposition of certain toxic compounds by halamine structures.

---

### Approach:

The controlled radical grafting reaction on fiber surfaces is a completely novel approach to functionalize most textile materials in conventional wet finishing processes. The desired functional groups can vary from antimicrobial, anti-chemical, anti-UV, antistatic, anti-irradiation and chromospheres, to many other potential groups. This radical grafting reaction is the only way to permanently incorporate these functional groups onto the surfaces of all potential fibers or fabrics. We have identified one reactive moiety that can undergo the radical grafting reaction but without forming homopolymers, and one initiator that can preferentially initiate radicals on fiber surfaces instead of monomers. However, we need to continue to explore this chemistry, understand the mechanisms

of the reactions, and explore other options to broaden the applications. Vinyl structures, such as allylic structures, that are self-inhibiting in chain propagation reactions will be employed in the research. To make the grafting fully controllable, mono-allylic and di-allylic groups or other groups that can provide different reactivity will be attached to functional groups such as hydantoin or melamine rings (Figure 2). Radical initiators such as t-butyl peroxide (Figure 2) that can form such radicals which prefer hydrogen abstraction reactions on fiber surfaces rather than addition reactions on monomers will be selected as well.

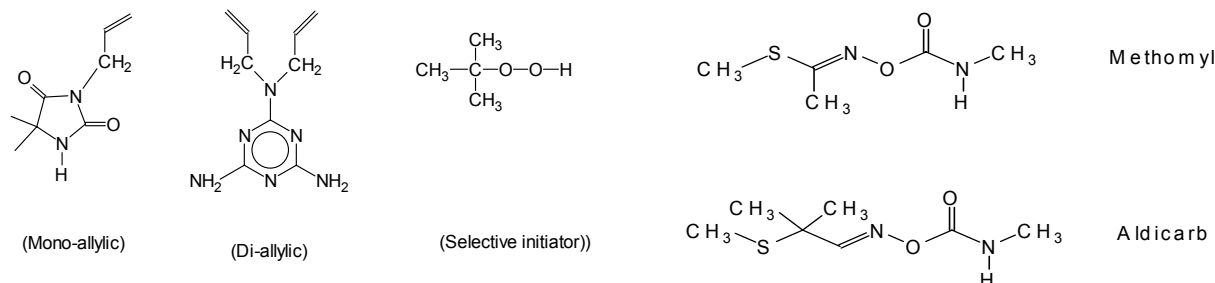


Figure 2 Structures of monomers, initiator, and pesticides

Evaluation of the desired functions on the grafted textiles will be continued in order to verify whether the radical grafting reactions would change the properties of the original functional groups. The biocidal properties of the chemically modified fabrics with the new monomers will be evaluated following AATCC test method 100. The focus of the research in this specific area will be on the following:

1. Increasing grafting yield on all textile materials, particularly on fabrics containing two or more different fibers.
2. Improving washing durability and storage stability of the grafted halamine structures

Detoxification of toxic chemicals will be started in this year with the halamine-containing fabrics. Some toxic pesticides such as methomyl and aldicarb, and toxic structures such as half mustard and cyanide groups will be employed in contact with halogenated Nomex fabrics. A detailed testing procedure is designed as following:

1. Quantitatively measure the active chlorine on the treated fabrics and cut the fabric into circular swatches (1-2 inches);
2. Expose an aqueous or methanol solution that contains a known amount of a toxic compound to a certain amount of fabric swatches in a closed container for a certain amount of time;
3. After a specified contact time, the swatches will be quenched by using a diluted sodium thiosulfate solution and the solution will be extracted with certain amount of ethyl acetate
4. The extraction solution will be concentrated by using a rotor evaporator or directly employed for quantitative analysis;
5. Gas chromatography (GC), GC-MS, and HPLC will be employed in the characterization of the toxic chemicals and their decomposed fragments.

---

#### Outreach to Industry:

This research has produced very positive preliminary results showing that the new finishing technology is highly feasible and practical to the functional textile finishing of many different fabrics. We will start to contact textile manufacturers such as fiber manufacturers, textile chemical formulators, chemical finishing mills, specialty fabric, and garment manufacturers for pilot trials.

---

#### New Resources Required:

We need to purchase a UV detector for detecting toxic compounds.